

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SONY CORP

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**(54) POSITIVE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTIC SECONDARY BATTERY USING THE SAME****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a positive active material in which capacity is high, cost is low, and an increase with passage of time in interface polarization resistance is small, and realize a nonaqueous electrolytic secondary battery with small internal resistance and high charge energy efficiency by using the positive active material.

**SOLUTION:** The surface of a nickel-containing, lithium-containing compound oxide is covered with a compound containing either one of Co, Al, and Mn. As the compound for covering the surfaces of the compound oxide particles, a metal alcoxide containing either one of Co, Al, and Mn is practically listed.

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CLAIMS

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[Claim(s)]

[Claim 1] $\text{LiNi}_x\text{M}_y\text{O}_2$  (however, M at least a kind of element chosen from aluminum, Mn, Fe, nickel, Co, Cr, Ti, Zn, P, and B) [ express and ]  $x \rightarrow 0 < x \leq 1$  and  $y \rightarrow 0 \leq y < 1$  -- it is -- positive active material which carries out coating treatment of the surface of compound oxide particles expressed with a compound of Co, aluminum, and Mn which contains either at least, and is characterized by things.

[Claim 2]The positive active material according to claim 1, wherein a compound which carries out coating treatment of the surface of compound oxide particles is a metal alkoxide containing Co, aluminum, or Mn.

[Claim 3]When  $z/(x+z)$  (however, x is an atomic composition ratio of nickel and z is the sum total of Co, aluminum, and an atomic composition ratio of Mn) is set to D in the surface of compound oxide particles, and  $z/(x+z)$  D (b) in (s) and the whole compound oxide particles,  $D(s) > D(b)$  The positive active material according to claim 1 fulfilling becoming conditions.

[Claim 4]The positive active material according to claim 1, wherein a compound which carries out coating treatment of the surface of compound oxide particles is a compound containing Co.

[Claim 5]The positive active material according to claim 4, wherein D (s) is  $1 \geq D(s) > 0.3$ .

[Claim 6] $\text{LiNi}_x\text{M}_y\text{O}_2$  (however, M at least a kind of element chosen from aluminum, Mn, Fe, nickel, Co, Cr, Ti, Zn, P, and B) [ express and ]  $x \rightarrow 0 < x \leq 1$  and  $y \rightarrow 0 \leq y < 1$  -- it is -- a nonaqueous electrolyte secondary battery with which it is expressed and the surface is characterized by using Co, aluminum, and compound oxide particles by which coating treatment was carried out with a compound of Mn which contains either at least as positive active material.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the positive active material used with a nonaqueous electrolyte secondary battery etc., and the nonaqueous electrolyte secondary battery using it.

[0002]

[Description of the Prior Art]In recent years, in connection with the rapid progress of various electronic equipment, research of the rechargeable battery is advanced as a portable power supply which can be used stability and economically for a long time.

[0003]As a typical rechargeable battery, a lead storage battery, an alkaline battery, a lithium secondary battery, etc. can be mentioned. Among these, research is actively made from the ability of the lithium secondary battery to attain high power and high energy density compared with other conventional rechargeable batteries, and the proposal is made with various composition. There are some with which practical use is already presented.

[0004]For example, generally as a negative electrode of a lithium secondary battery, a dope, the material which can be dedoped, metal lithium, or a lithium alloy is used in lithium. Considering lithium as a dope and a material which can be dedoped, a conductive polymer or laminar compounds (a carbon material, a metallic oxide, etc.) etc. which doped lithium are proposed.

[0005]On the other hand, as positive active material which constitutes an anode, a metallic oxide, metallic sulfide, and specific polymer can be used. Specifically, the compound which does not contain lithium, such as  $\text{TiS}_2$ ,  $\text{MoS}_2$ ,  $\text{NbSe}_2$ , and  $\text{V}_2\text{O}_5$ , and the multiple oxide which contains lithium like  $\text{LiMO}_2$  (however, M is Co, nickel, Mn, Fe, etc.) are mentioned. Especially, the lithium content multiple oxide containing nickel is expected from capacity being large and being comparatively cheap. These compounds can also mix and use two or more sorts besides single use.

[0006]High polymer films, such as polypropylene, are used as a separator made to intervene between a negative electrode and an anode. In this case, from a point of the conductivity and the energy density of a lithium ion, to make it as thin as possible is needed and a high polymer film is 50 micrometers or less practical.

[0007]And what dissolved lithium salt, such as  $\text{LiPF}_6$ , in the nonaqueous solvent which makes a subject high dielectric constant solvents, such as propylene carbonate, as electrolyte salt as an electrolysis solution is used.

[0008]

[Problem(s) to be Solved by the Invention]By the way, generally by a cell, a part of energy which is inherent with the internal resistance is consumed. Therefore, in order to use the charged energy efficiently, it can be said that it is more desirable as internal resistance is low.

[0009]The internal resistance of a cell mainly originates in the resistance in an active material, and the resistance (interfacial polarization resistance is called hereafter) generated in the interface of an active material particle and an electrolysis solution, and what doubled these resistance is equivalent to the internal resistance of the whole cell.

[0010]Here, in the lithium content multiple oxide previously illustrated as positive active material, the phenomenon in which this interfacial polarization resistance increases temporally is seen. Although it has the strong point in which the lithium content multiple oxide which contains nickel especially has large comparatively cheap capacity, compared with  $\text{LiCoO}_2$  etc., the tendency for the temporal increase in this interfacial resistance to be comparatively large is one of the demerits.

[0011]Then, this invention is proposed in view of such the conventional actual condition, and is a thing.

The purpose is to provide positive active material with few temporal increases in \*\*.

Internal resistance aims it small to let charging energy provide the nonaqueous electrolyte secondary battery used efficiently by using such positive active material.

[0012]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, as a result of this invention person's etc. repeating examination wholeheartedly, near the surface of a lithium content multiple oxide containing nickel, When it was made to make either Co, aluminum or Mn exist in high concentration to nickel as a solid state, it came to acquire knowledge that an increase in temporal interfacial polarization resistance in this multiple oxide is suppressed.

[0013]Positive active material of this invention is completed based on such knowledge,  $\text{LiNi}_x\text{M}_y\text{O}_2$  (however, M at least a kind of element chosen from aluminum, Mn, Fe, nickel, Co, Cr, Ti, Zn, P, and B) [ express and ]  $x \rightarrow 0 < x \leq 1$  and  $y \rightarrow 0 \leq y < 1$  — it is — coating treatment of the surface of compound oxide particles expressed is carried out with a compound of Co, aluminum, and Mn which contains either at least.

[0014]As a compound used in order to cover this compound-oxide-particles surface, a metal alkoxide etc. which specifically contain Co, aluminum, or Mn are mentioned. A compound which contains Co as a compound used for coating treatment is preferred.

[0015] $z/[(x+z)]$  in / it becomes a form where a compound which contains Co, aluminum, and Mn in a particle surface adhered when coating treatment of the compound-oxide-particles surface was carried out with these compounds, and / the surface of compound oxide particles ]  $(x+z)$  (however, x is an atomic composition ratio of nickel and z is the sum total of Co, aluminum, and an atomic composition ratio of Mn.) here — this value —  $D(s)$  — carrying out —  $z/(x+z)$  (here, this value is set to  $D(b)$ ) in the whole compound oxide particles — size — it becomes a value. As for  $D(s)$ , when using a thing containing Co as a compound for processing especially, it is desirable that it is  $1 \geq D(s) > 0.3$ .

[0016]

[Embodiment of the Invention]Hereafter, the concrete embodiment of this invention is described.

[0017]The positive active material of this invention  $\text{LiNi}_x\text{M}_y\text{O}_2$ . (However, M at least a kind of element chosen from aluminum, Mn, Fe, nickel, Co, Cr, Ti, Zn, P, and B) [ express and ]  $x \rightarrow 0 < x \leq 1$  and  $y \rightarrow 0 \leq y < 1$  — it is — it has come to carry out coating treatment of the surface of the compound oxide particles expressed with the compound of Co, aluminum, and Mn which contains either at least. That is, the compound containing Co, aluminum, or Mn adheres to the lithium compound-oxide-particles surface containing nickel, and the above-mentioned positive active material has become a form where surface treatment of the particles was carried out by this.

[0018]In the compound oxide particles to which such surface treatment was given, the rate that nickel occupies in the part and the surface on which the compound containing Co, aluminum, or Mn adhered to the surface is decreasing. The temporal increase in interfacial polarization resistance is suppressed because the rate that this nickel occupies decreased. Therefore, having the strong point of the compound oxide particles containing high capacity and nickel of being cheap, moreover internal resistance of a cell is not increased and the characteristic outstanding as positive active material is obtained.

[0019]As a compound for processing, the metal alkoxide of Co, aluminum, or Mn, etc. are mentioned, for example. Among these, in order to perform surface treatment of compound oxide

particles, for example by Co alkoxide, the compound oxide particles used as a processed object will be saved about one day after an injection and stirring at the surface treating liquid which dissolved Co alkoxide. During preservation, combination of  $-O-Co-O$  generates and a layer with high Co concentration is formed in the compound-oxide-particles surface. Supernatant liquor is thrown away after preservation and a solvent washes residual particles several times. And the compound oxide particles by which surface treatment was carried out are obtained by drying this particle. Surface treatment by aluminum alkoxide and Mn alkoxide is also performed according to this.

[0020]As a compound for processing, it may be a conjugated compound of the thing, i.e., Li and Mn, having contained Li, aluminum, or Co.

[0021]It is desirable to use the thing containing Co as a compound for processing. In aluminum or Mn, when it dissolves to compound oxide particles, the capacity of a cell is committed in the direction decreased a little, but it is because most capacity of a cell is not decreased in Co.

[0022]Thus, in the compound oxide particles to which surface treatment was performed, the concentration of Co, aluminum, or Mn becomes large in a particle surface rather than the whole particle. That is, when  $z/(x+z)$  (however,  $x$  is an atomic composition ratio of nickel and  $z$  is the sum total of Co, aluminum, and the atomic composition ratio of Mn) is set to  $D$  in the surface, and  $z/(x+z)$   $D$  (b) in (s) and the whole particle, the value of  $D$  (s) turns into a value as for which size becomes rather than the value of  $D$  (b). As for the value of  $D$  (s), when using the thing containing Co as a compound for processing especially, it is desirable that it is  $1 \geq D(s) > 0.3$ . When  $D$  (s) is 0.3 or less, the temporal increase in the interfacial resistance of compound oxide particles cannot fully be lowered.

[0023]This  $D$  (s) and  $D$  (b) are values calculated as follows, respectively.

[0024]Measurement of  $D$  (s): 50-cc weighing of the 0.1M HCl solution is carried out, and under ordinary temperature, 500 mg of granular materials are fed into this HCl solution, and it is immersed for 5 minutes under the room temperature of 23 \*\*. Thereby, the surface of a granular material is dissolved by acid. Next, the residue powder which remained without dissolving from HCl solution is removed. And only the HCl solution which remained as supernatant liquor is analyzed by ICP-AES (inductively coupled plasma-atomic emission spectroscopy), The quantitative ratio of nickel which exists in a solution, Co and aluminum, or Mn is measured, and  $z/(x+z)$  is computed based on the measurand.

[0025]Measurement of  $D$  (b): Feed 500 mg of granular materials into 1M HCl solution, and dissolve the whole granular material in it. And the HCl solution in which the granular material was dissolved is analyzed by ICP-AES, the quantitative ratio of nickel which exists in a solution, Co and aluminum, or Mn is measured, and  $z/(x+z)$  is computed based on the measurand.

[0026]The compound oxide particles to which the above surface treatment was given are used for the anode of a nonaqueous electrolyte secondary battery.

[0027]In order to form an anode by the above-mentioned compound oxide particles, these compound oxide particles and conducting agent \*\*\*\*\* are mixed, positive electrode mixture is prepared, and compression molding of this positive electrode mixture is carried out to desired electrode shape. Here, it is [ binder / a conducting agent or ] usable in each thing usually used by this kind of cell.

[0028]The negative electrode and nonaqueous electrolyte which are used combining the above-mentioned anode may also be too used by this kind of cell.

[0029]For example, as an active material of a negative electrode, a dope and the material which can be dedoped are used in lithium besides lithium alloys, such as metal lithium or a lithium aluminum alloy. Lithium as a dope and a material which can be dedoped, for example, pyrolytic carbon and corks (pitch coke and needle coke.) Polymer, such as carbonaceous materials, such as graphite, glassy carbon, an organic polymer compound baking body (what calcinated and carbonized phenol resin, furan resin, etc. at a suitable temperature) and carbon fiber, such as petroleum coke, and activated carbon, or polyacethylene, and polypyrrole, etc. can be used.

[0030]In order to form a negative electrode by such a carbonaceous material and polymer, a binder is mixed with these materials, negative electrode mixture is prepared, and compression molding of this negative electrode mixture is carried out to desired electrode shape.

[0031]On the other hand as a nonaqueous solvent of nonaqueous electrolyte, for example Propylene carbonate, Ethylene carbonate, butylene carbonate, vinylene carbonate, Gamma-butyrolactone, sulfolane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 2-methyltetrahydrofuran, 3-methyl-1,3-dioxolane, methyl propionate, methyl butyrate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, etc. can be used. It is preferred to use chain carbonate, such as cyclic carbonate, such as propylene carbonate and vinylene carbonate, dimethyl carbonate, diethyl carbonate, and dipropyl carbonate, for voltage from a stable point especially. Even if it uses these nonaqueous solvents alone, respectively and uses them combining two or more kinds, they are not cared about.

[0032]As electrolyte salt in which a nonaqueous solvent is dissolved,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , etc. can be used. Among these, it is preferred to use  $\text{LiPF}_6$  and  $\text{LiBF}_4$  especially.

[0033]It may be made to use a solid electrolyte instead of nonaqueous electrolyte in this cell.

[0034]the shape in particular of a cell is not limited but can be made into shape at versatility, such as cylindrical, a square shape, a coin type, and a button type.

[0035]

[Example]Hereafter, the example of this invention is described based on an experimental result.

[0036]As it was the primary example, positive active material was generated.

[0037]First, the compound oxide particles and surface treating liquid which are shown below were prepared.

[0038]Compound oxide particles (processed object) :  $\text{CoO}$ ,  $\text{NiO}$ , and  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder surface treating liquid:Co isopropoxide obtained by mixing so that it may be set to Li:nickel:Co=1:0.8:0.2 (mol ratio), and heat-treating at the temperature of 700–800 \*\* among the atmosphere for 10 hours [ $\text{Co}(\text{O}-i-\text{C}_3\text{H}_7)_2$ ] 1g ( $5.6 \times 10^{-3}$ mol considerable amount) \*\*\*\* picking.

The compound oxide particles 2g were supplied to the above-mentioned surface treating liquid under Co alkoxide solution nitrogen atmosphere dissolved in 2-ethoxyethanol ( $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$ ) 100cc, and after carrying out mixed stirring, it saved at ordinary temperature for 24 hours. Supernatant liquor was thrown away after preservation and residual particles were washed several times by 2-ethoxyethanol. And the compound oxide particles (positive active material) by which surface treatment was carried out were obtained by heating this particle at the temperature of 300–800 \*\* in the atmosphere after desiccation.

[0039]D (s) and D (b) were measured by the extraction test of 0.1MHCl or 1MHCl about unsettled compound oxide particles and the compound oxide particles to which the surface treatment was performed. The result is shown in Table 1.

[0040]

[Table 1]

	D ( s )	D ( b )
処理済複合酸化物粒子	0 . 3 4	0 . 2 5
未処理複合酸化物粒子	0 . 2 6	0 . 2 5

[0041]As shown in Table 1, the value of D (s) is increasing the compound oxide particles to which the surface treatment was performed from unsettled compound oxide particles. From this, it was checked that the Co concentration on the surface of compound oxide particles had increased by this surface treatment.

[0042]Next, the coin type cell was produced by using as positive active material the compound oxide particles by which surface treatment was made as mentioned above.

[0043]Graphite 7 weight section and fluorine system high polymer binder 3 weight section were added to the compound-oxide-particles 90 above-mentioned weight section, and positive

electrode mixture was prepared by mixing with dimethylformamide (DMF). After volatilizing thoroughly DMF which is a solvent by drying this positive electrode mixture enough, the disc-like positive electrode of surface area  $2$  of about 2 cm was produced for those about 60 mg by \*\*\*\* picking and carrying out application-of-pressure molding.

[0044]On the other hand, the negative electrode produced Li rolling metal by piercing disc-like.

[0045]The amount of Li(s) of this negative electrode is several 100 times the maximum charging capacity of an anode, and does not restrict the electrochemical performance of an anode.

[0046]The anode and negative electrode which were produced as mentioned above were stored to the positive electrode can and the negative electrode can, respectively, and it laminated on both sides of the separator in between. And the electrolysis solution made to dissolve  $\text{LiPF}_6$  in propylene carbonate (PC) was poured in into the can, and the coin type cell was produced by carrying out caulking sealing of a positive electrode can and the negative electrode can via a gasket. and -- this cell -- charge and discharge current density  $0.5 \text{ mA/cm}^2$  -- it charged until OCV (open-circuit voltage) turned into 4.2V on conditions.

[0047]Except having used aluminum( $\text{OCH}_3$ ) $_3$  as a metal alkoxide which dissolves in the surface treating liquid of example 2 compound oxide particles, positive active material was generated like Example 1, and the coin type cell was produced. and -- this cell -- charge and discharge current density  $0.5 \text{ mA/cm}^2$  -- it charged until OCV (open-circuit voltage) turned into 4.2V on conditions.

[0048]Except having used  $\text{Mn}(\text{O}-i-\text{C}_3\text{H}_7)_2$  as a metal alkoxide which dissolves in the surface treating liquid of example 3 compound oxide particles, positive active material was generated like Example 1, and the coin type cell was produced. and -- this cell -- charge and discharge current density  $0.5 \text{ mA/cm}^2$  -- it charged until OCV (open-circuit voltage) turned into 4.2V on conditions.

[0049]The coin type cell was produced like Example 1 except having used the compound oxide particles which have not performed comparative example 1 surface treatment as positive active material as it was. and -- this cell -- charge and discharge current density  $0.5 \text{ mA/cm}^2$  -- it charged until OCV (open-circuit voltage) turned into 4.2V on conditions.

[0050]About the cell produced as mentioned above, complex impedance measurement was performed every 12 hours, and the interfacial polarization resistance in a positive electrode surface was estimated from Cole-Cole plot calculated. The measuring condition of complex impedance is as follows.

[0051]measurement use model: -- H.P.4192 A Impedance Analyzer temperature: -- ordinary temperature (23 \*\*)

frequency range: -- 0.5 Hz - 1000-Hz impression bias voltage: -- 4.2V maximum current: -- 10-mA time-between-measurements: -- aging of \*\* \*\*\*\* interfacial polarization resistance is shown in drawing 1 for the 12 whole hours. In drawing 1, a vertical axis is the value which standardized interfacial polarization resistance  $R_t$  t-hour after a measurement start by interfacial polarization resistance  $R_{t=0}$  at the time of a measurement start.

[0052]The cell of Example 1 - Example 3 used for the anode the compound oxide particles to which the surface treatment was performed by the metal alkoxide of Co, aluminum, or Mn so that drawing 1 may show, Compared with the cell of the comparative example 1 which used unsettled compound oxide particles for the anode, the temporal increase in the interfacial polarization resistance in a positive electrode surface is controlled.

[0053]In the nonaqueous electrolyte secondary battery, in the interfacial polarization resistance between the compound oxide particles concerned and electrolysis solution not increasing easily, it turned out that it is effective to process the compound oxide particles containing nickel from this with the compound containing Co, aluminum, and Mn.

[0054]

[Effect of the Invention]So that clearly also from the above explanation the positive active material of this invention,  $\text{LiNi}_x\text{M}_y\text{O}_2$  (however, M at least a kind of element chosen from

aluminum, Mn, Fe, nickel, Co, Cr, Ti, Zn, P, and B) [ express and ]  $x$  --  $0 < x \leq 1$  and  $y$  --  $0 \leq y < 1$  -- it is -- since coating treatment of the surface of the compound oxide particles expressed is carried out with Co, aluminum, and the compound containing any at least one sort of Mn -- high capacity -- while it is cheap, there are few temporal increases in interfacial polarization resistance. Therefore, by using such positive active material, internal resistance is small and the nonaqueous electrolyte secondary battery with which charging energy is used efficiently can be realized.

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[Description of the Prior Art]In recent years, in connection with the rapid progress of various electronic equipment, research of the rechargeable battery is advanced as a portable power supply which can be used stability and economically for a long time.

[0003]As a typical rechargeable battery, a lead storage battery, an alkaline battery, a lithium secondary battery, etc. can be mentioned. Among these, research is actively made from the ability of the lithium secondary battery to attain high power and high energy density compared with other conventional rechargeable batteries, and the proposal is made with various composition. There are some with which practical use is already presented.

[0004]For example, generally as a negative electrode of a lithium secondary battery, a dope, the material which can be dedoped, metal lithium, or a lithium alloy is used in lithium. Considering lithium as a dope and a material which can be dedoped, a conductive polymer or laminar compounds (a carbon material, a metallic oxide, etc.) etc. which doped lithium are proposed.

[0005]On the other hand, as positive active material which constitutes an anode, a metallic oxide, metallic sulfide, and specific polymer can be used. Specifically, the compound which does not contain lithium, such as  $\text{TiS}_2$ ,  $\text{MoS}_2$ ,  $\text{NbSe}_2$ , and  $\text{V}_2\text{O}_5$ , and the multiple oxide which contains lithium like  $\text{LiMO}_2$  (however, M is Co, nickel, Mn, Fe, etc.) are mentioned. Especially, the lithium content multiple oxide containing nickel is expected from capacity being large and being comparatively cheap. These compounds can also mix and use two or more sorts besides single use.

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[0010]Here, in the lithium content multiple oxide previously illustrated as positive active material, the phenomenon in which this interfacial polarization resistance increases temporally is seen. Although it has the strong point in which the lithium content multiple oxide which contains nickel especially has large comparatively cheap capacity, compared with  $\text{LiCoO}_2$  etc., the tendency for the temporal increase in this interfacial resistance to be comparatively large is one of the demerits.

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[Means for Solving the Problem]In order to attain the above-mentioned purpose, as a result of this invention person's etc. repeating examination wholeheartedly, near the surface of a lithium content multiple oxide containing nickel, When it was made to make either Co, aluminum or Mn exist in high concentration to nickel as a solid state, it came to acquire knowledge that an increase in temporal interfacial polarization resistance in this multiple oxide is suppressed.

[0013]Positive active material of this invention is completed based on such knowledge,  $\text{LiNi}_x\text{M}_y\text{O}_2$  (however, M at least a kind of element chosen from aluminum, Mn, Fe, nickel, Co, Cr, Ti, Zn, P, and B) [ express and ]  $x \rightarrow 0 < x \leq 1$  and  $y \rightarrow 0 \leq y < 1$  — it is — coating treatment of the surface of compound oxide particles expressed is carried out with a compound of Co, aluminum, and Mn which contains either at least.

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[Embodiment of the Invention]Hereafter, the concrete embodiment of this invention is described.

[0017]The positive active material of this invention  $\text{LiNi}_x\text{M}_y\text{O}_2$ . (However, M at least a kind of element chosen from aluminum, Mn, Fe, nickel, Co, Cr, Ti, Zn, P, and B) [ express and ]  $x \rightarrow 0 < x \leq 1$  and  $y \rightarrow 0 \leq y < 1$  — it is — it has come to carry out coating treatment of the surface of the compound oxide particles expressed with the compound of Co, aluminum, and Mn which contains either at least. That is, the compound containing Co, aluminum, or Mn adheres to the lithium compound-oxide-particles surface containing nickel, and the above-mentioned positive active material has become a form where surface treatment of the particles was carried out by this.

[0018]In the compound oxide particles to which such surface treatment was given, the rate that nickel occupies in the part and the surface on which the compound containing Co, aluminum, or Mn adhered to the surface is decreasing. The temporal increase in interfacial polarization resistance is suppressed because the rate that this nickel occupies decreased. Therefore, having the strong point of the compound oxide particles containing high capacity and nickel of being cheap, moreover internal resistance of a cell is not increased and the characteristic outstanding as positive active material is obtained.

[0019]As a compound for processing, the metal alkoxide of Co, aluminum, or Mn, etc. are mentioned, for example. Among these, in order to perform surface treatment of compound oxide

particles, for example by Co alkoxide, the compound oxide particles used as a processed object will be saved about one day after an injection and stirring at the surface treating liquid which dissolved Co alkoxide. During preservation, combination of  $-O-Co-O$  generates and a layer with high Co concentration is formed in the compound-oxide-particles surface. Supernatant liquor is thrown away after preservation and a solvent washes residual particles several times. And the compound oxide particles by which surface treatment was carried out are obtained by drying this particle. Surface treatment by aluminum alkoxide and Mn alkoxide is also performed according to this.

[0020]As a compound for processing, it may be a conjugated compound of the thing, i.e., Li and Mn, having contained Li, aluminum, or Co.

[0021]It is desirable to use the thing containing Co as a compound for processing. In aluminum or Mn, when it dissolves to compound oxide particles, the capacity of a cell is committed in the direction decreased a little, but it is because most capacity of a cell is not decreased in Co.

[0022]Thus, in the compound oxide particles to which surface treatment was performed, the concentration of Co, aluminum, or Mn becomes large in a particle surface rather than the whole particle. That is, when  $z/(x+z)$  (however,  $x$  is an atomic composition ratio of nickel and  $z$  is the sum total of Co, aluminum, and the atomic composition ratio of Mn) is set to  $D$  in the surface, and  $z/(x+z)$   $D$  (b) in (s) and the whole particle, the value of  $D$  (s) turns into a value as for which size becomes rather than the value of  $D$  (b). As for the value of  $D$  (s), when using the thing containing Co as a compound for processing especially, it is desirable that it is  $1 \geq D(s) > 0.3$ . When  $D$  (s) is 0.3 or less, the temporal increase in the interfacial resistance of compound oxide particles cannot fully be lowered.

[0023]This  $D$  (s) and  $D$  (b) are values calculated as follows, respectively.

[0024]Measurement of  $D$  (s): 50-cc weighing of the 0.1M HCl solution is carried out, and under ordinary temperature, 500 mg of granular materials are fed into this HCl solution, and it is immersed for 5 minutes under the room temperature of 23 \*\*. Thereby, the surface of a granular material is dissolved by acid. Next, the residue powder which remained without dissolving from HCl solution is removed. And only the HCl solution which remained as supernatant liquor is analyzed by ICP-AES (inductively coupled plasma-atomic emission spectroscopy). The quantitative ratio of nickel which exists in a solution, Co and aluminum, or Mn is measured, and  $z/(x+z)$  is computed based on the measurand.

[0025]Measurement of  $D$  (b): Feed 500 mg of granular materials into 1M HCl solution, and dissolve the whole granular material in it. And the HCl solution in which the granular material was dissolved is analyzed by ICP-AES, the quantitative ratio of nickel which exists in a solution, Co and aluminum, or Mn is measured, and  $z/(x+z)$  is computed based on the measurand.

[0026]The compound oxide particles to which the above surface treatment was given are used for the anode of a nonaqueous electrolyte secondary battery.

[0027]In order to form an anode by the above-mentioned compound oxide particles, these compound oxide particles and conducting agent \*\*\*\*\* are mixed, positive electrode mixture is prepared, and compression molding of this positive electrode mixture is carried out to desired electrode shape. Here, it is [ binder / a conducting agent or ] usable in each thing usually used by this kind of cell.

[0028]The negative electrode and nonaqueous electrolyte which are used combining the above-mentioned anode may also be too used by this kind of cell.

[0029]For example, as an active material of a negative electrode, a dope and the material which can be dedoped are used in lithium besides lithium alloys, such as metal lithium or a lithium aluminum alloy. Lithium as a dope and a material which can be dedoped, for example, pyrolytic carbon and corks (pitch coke and needle coke.) Polymer, such as carbonaceous materials, such as graphite, glassy carbon, an organic polymer compound baking body (what calcinated and carbonized phenol resin, furan resin, etc. at a suitable temperature) and carbon fiber, such as petroleum coke, and activated carbon, or polyacethylene, and polypyrrole, etc. can be used.

[0030]In order to form a negative electrode by such a carbonaceous material and polymer, a binder is mixed with these materials, negative electrode mixture is prepared, and compression molding of this negative electrode mixture is carried out to desired electrode shape.

[0031]On the other hand as a nonaqueous solvent of nonaqueous electrolyte, for example Propylene carbonate, Ethylene carbonate, butylene carbonate, vinylene carbonate, Gamma-butyrolactone, sulfolane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 2-methyltetrahydrofuran, 3-methyl-1,3-dioxolane, methyl propionate, methyl butyrate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, etc. can be used. It is preferred to use chain carbonate, such as cyclic carbonate, such as propylene carbonate and vinylene carbonate, dimethyl carbonate, diethyl carbonate, and dipropyl carbonate, for voltage from a stable point especially. Even if it uses these nonaqueous solvents alone, respectively and uses them combining two or more kinds, they are not cared about.

[0032]As electrolyte salt in which a nonaqueous solvent is dissolved,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , etc. can be used, Among these, it is preferred to use  $\text{LiPF}_6$  and  $\text{LiBF}_4$  especially.

[0033]It may be made to use a solid electrolyte instead of nonaqueous electrolyte in this cell.

[0034]the shape in particular of a cell is not limited but can be made into shape at versatility, such as cylindrical, a square shape, a coin type, and a button type.

[0035]

[Example]Hereafter, the example of this invention is described based on an experimental result.

[0036]As it was the primary example, positive active material was generated.

[0037]First, the compound oxide particles and surface treating liquid which are shown below were prepared.

[0038]Compound oxide particles (processed object) :  $\text{CoO}$ ,  $\text{NiO}$ , and  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder surface treating liquid:Co isopropoxide obtained by mixing so that it may be set to Li:nickel:Co=1:0.8:0.2 (mol ratio), and heat-treating at the temperature of 700–800 \*\* among the atmosphere for 10 hours [ $\text{Co}(\text{O}-i-\text{C}_3\text{H}_7)_2$ ] 1g ( $5.6 \times 10^{-3}$ mol considerable amount) \*\*\*\* picking, The compound oxide particles 2g were supplied to the above-mentioned surface treating liquid under Co alkoxide solution nitrogen atmosphere dissolved in 2-ethoxyethanol ( $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$ ) 100cc, and after carrying out mixed stirring, it saved at ordinary temperature for 24 hours. Supernatant liquor was thrown away after preservation and residual particles were washed several times by 2-ethoxyethanol. And the compound oxide particles (positive active material) by which surface treatment was carried out were obtained by heating this particle at the temperature of 300–800 \*\* in the atmosphere after desiccation.

[0039]D (s) and D (b) were measured by the extraction test of 0.1MHCl or 1MHCl about unsettled compound oxide particles and the compound oxide particles to which the surface treatment was performed. The result is shown in Table 1.

[0040]

[Table 1]

	D ( s )	D ( b )
処理済複合酸化物粒子	0 . 3 4	0 . 2 5
未処理複合酸化物粒子	0 . 2 6	0 . 2 5

[0041]As shown in Table 1, the value of D (s) is increasing the compound oxide particles to which the surface treatment was performed from unsettled compound oxide particles. From this, it was checked that the Co concentration on the surface of compound oxide particles had increased by this surface treatment.

[0042]Next, the coin type cell was produced by using as positive active material the compound oxide particles by which surface treatment was made as mentioned above.

[0043]Graphite 7 weight section and fluorine system high polymer binder 3 weight section were added to the compound-oxide-particles 90 above-mentioned weight section, and positive

electrode mixture was prepared by mixing with dimethylformamide (DMF). After volatilizing thoroughly DMF which is a solvent by drying this positive electrode mixture enough, the disc-like positive electrode of surface area <sup>2</sup> of about 2 cm was produced for those about 60 mg by \*\*\*\* picking and carrying out application-of-pressure molding.

[0044]On the other hand, the negative electrode produced Li rolling metal by piercing disc-like.

[0045]The amount of Li(s) of this negative electrode is several 100 times the maximum charging capacity of an anode, and does not restrict the electrochemical performance of an anode.

[0046]The anode and negative electrode which were produced as mentioned above were stored to the positive electrode can and the negative electrode can, respectively, and it laminated on both sides of the separator in between. And the electrolysis solution made to dissolve  $\text{LiPF}_6$  in propylene carbonate (PC) was poured in into the can, and the coin type cell was produced by carrying out caulking sealing of a positive electrode can and the negative electrode can via a gasket. and -- this cell -- charge and discharge current density  $0.5 \text{ mA/cm}^2$  -- it charged until OCV (open-circuit voltage) turned into 4.2V on conditions.

[0047]Except having used aluminum( $\text{OCH}_3$ )<sub>3</sub> as a metal alkoxide which dissolves in the surface treating liquid of example 2 compound oxide particles, positive active material was generated like Example 1, and the coin type cell was produced. and -- this cell -- charge and discharge current density  $0.5 \text{ mA/cm}^2$  -- it charged until OCV (open-circuit voltage) turned into 4.2V on conditions.

[0048]Except having used  $\text{Mn}(\text{O}-i-\text{C}_3\text{H}_7)_2$  as a metal alkoxide which dissolves in the surface treating liquid of example 3 compound oxide particles, positive active material was generated like Example 1, and the coin type cell was produced. and -- this cell -- charge and discharge current density  $0.5 \text{ mA/cm}^2$  -- it charged until OCV (open-circuit voltage) turned into 4.2V on conditions.

[0049]The coin type cell was produced like Example 1 except having used the compound oxide particles which have not performed comparative example 1 surface treatment as positive active material as it was. and -- this cell -- charge and discharge current density  $0.5 \text{ mA/cm}^2$  -- it charged until OCV (open-circuit voltage) turned into 4.2V on conditions.

[0050>About the cell produced as mentioned above, complex impedance measurement was performed every 12 hours, and the interfacial polarization resistance in a positive electrode surface was estimated from Cole-Cole plot calculated. The measuring condition of complex impedance is as follows.

[0051]measurement use model: -- H.P.4192 A Impedance Analyzer temperature: -- ordinary temperature (23 \*\*)

frequency range: -- 0.5 Hz - 1000-Hz impression bias voltage: -- 4.2V maximum current: -- 10-mA time-between-measurements: -- aging of \*\* \*\*\*\* interfacial polarization resistance is shown in drawing 1 for the 12 whole hours. In drawing 1, a vertical axis is the value which standardized interfacial polarization resistance  $R_t$  t-hour after a measurement start by interfacial polarization resistance  $R_{t=0}$  at the time of a measurement start.

[0052]The cell of Example 1 - Example 3 used for the anode the compound oxide particles to which the surface treatment was performed by the metal alkoxide of Co, aluminum, or Mn so that drawing 1 may show, Compared with the cell of the comparative example 1 which used unsettled compound oxide particles for the anode, the temporal increase in the interfacial polarization resistance in a positive electrode surface is controlled.

[0053]In the nonaqueous electrolyte secondary battery, in the interfacial polarization resistance between the compound oxide particles concerned and electrolysis solution not increasing easily, it turned out that it is effective to process the compound oxide particles containing nickel from this with the compound containing Co, aluminum, and Mn.

[0054]

[Effect of the Invention]So that clearly also from the above explanation the positive active material of this invention,  $\text{LiNi}_x\text{M}_y\text{O}_2$  (however, M at least a kind of element chosen from

aluminum, Mn, Fe, nickel, Co, Cr, Ti, Zn, P, and B) [ express and ]  $x \rightarrow 0 < x \leq 1$  and  $y \rightarrow 0 \leq y < 1$  — it is — since coating treatment of the surface of the compound oxide particles expressed is carried out with Co, aluminum, and the compound containing any at least one sort of Mn — high capacity — while it is cheap, there are few temporal increases in interfacial polarization resistance. Therefore, by using such positive active material, internal resistance is small and the nonaqueous electrolyte secondary battery with which charging energy is used efficiently can be realized.

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[Translation done.]

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1]It is a characteristic figure showing aging of the interfacial polarization resistance in a positive electrode surface.

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(54)【発明の名称】 正極活物質及びそれを用いた非水電解質二次電池

(57)【要約】

【課題】 高容量、安価であるとともに界面分極抵抗の経時的な増加が小さい正極活物質を提供する。また、そのような正極活物質を用いることで、内部抵抗が小さく、充電エネルギーが効率良く使用される非水電解質二次電池を実現する。

【解決手段】 Niを含有するリチウム含有複合酸化物の表面を、Co, Al, Mnのいずれかを含有する化合物によって被覆処理する。この複合酸化物粒子表面を被覆処理する化合物としては、具体的にはCo, Al, Mnのいずれかを含有する金属アルコキシドが挙げられる。



## 【特許請求の範囲】

【請求項1】  $\text{LiNi}_x\text{M}_y\text{O}_2$  (但し、MはAl, Mn, Fe, Ni, Co, Cr, Ti, Zn, P, Bから選ばれる少なくとも一種の元素を表し、 $x$ は $0 < x \leq 1$ 、 $y$ は $0 \leq y < 1$ である) で表される複合酸化物粒子の表面を、Co, Al, Mnの少なくともいずれかを含有する化合物によって被覆処理してなることを特徴とする正極活物質。

【請求項2】 複合酸化物粒子の表面を被覆処理する化合物は、Co, Al, Mnのいずれかを含有する金属アルコキシドであることを特徴とする請求項1記載の正極活物質。

【請求項3】 複合酸化物粒子の表面における  $z/(x+z)$  (但し、 $x$ はNiの原子組成比であり、 $z$ はCo, Al, Mnの原子組成比の合計である) をD(s)、複合酸化物粒子全体における  $z/(x+z)$  をD(b)としたときに、 $D(s) > D(b)$  なる条件を満たすことを特徴とする請求項1記載の正極活物質。

【請求項4】 複合酸化物粒子の表面を被覆処理する化合物は、Coを含有する化合物であることを特徴とする請求項1記載の正極活物質。

【請求項5】  $D(s)$  が、 $1 \geq D(s) > 0.3$  であることを特徴とする請求項4記載の正極活物質。

【請求項6】  $\text{LiNi}_x\text{M}_y\text{O}_2$  (但し、MはAl, Mn, Fe, Ni, Co, Cr, Ti, Zn, P, Bから選ばれる少なくとも一種の元素を表し、 $x$ は $0 < x \leq 1$ 、 $y$ は $0 \leq y < 1$ である) で表され、表面がCo, Al, Mnの少なくともいずれかを含有する化合物によって被覆処理された複合酸化物粒子を正極活物質として用いることを特徴とする非水電解質二次電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、非水電解質二次電池等で用いられる正極活物質及びそれをを用いた非水電解質二次電池に関する。

## 【0002】

【従来の技術】 近年、種々の電子機器の飛躍的進歩に伴い、長時間安定にかつ経済的に使用できるポータブル電源として、二次電池の研究が進められている。

【0003】 代表的な二次電池としては、鉛蓄電池、アルカリ蓄電池、リチウム二次電池等を挙げることができる。このうちリチウム二次電池は、従来の他の二次電池に比べて高出力、高エネルギー密度を達成できることから活発に研究がなされ、種々の構成で提案がなされている。また、既に実用に供されているものもある。

【0004】 たとえば、リチウム二次電池の負極としては、一般に、リチウムをドーブ・脱ドーブできる材料、金属リチウムまたはリチウム合金が使用される。リチウムをドーブ・脱ドーブできる材料としては、リチウムをドーブした導電性高分子もしくは層状化合物(炭素材

料、金属酸化物等) などが提案されている。

【0005】 一方、正極を構成する正極活物質としては、金属酸化物、金属硫化物、特定のポリマーが使用できる。具体的には、 $\text{TiS}_2$ 、 $\text{MoS}_2$ 、 $\text{NbSe}_2$ 、 $\text{V}_2\text{O}_5$ 等のリチウムを含有しない化合物や、 $\text{LiMO}_2$  (但し、MはCo, Ni, Mn, Fe等である) のようにリチウムを含有している複合酸化物が挙げられる。なかでも、Niを含むリチウム含有複合酸化物は、容量が大きく、比較的安価であることから期待されている。なお、これらの化合物は単独使用の他、複数種を混合して使用することもできる。

【0006】 また、負極と正極の間に介在させるセパレータとしては、ポリプロピレン等の高分子フィルムが使用される。この場合、リチウムイオンの伝導度とエネルギー密度の点から、高分子フィルムは可能な限り薄くすることが必要とされ、実用的には $50\mu\text{m}$ 以下である。

【0007】 そして、電解液としては、プロピレンカーボネート等の高誘電率溶媒を主体とする非水溶媒に、 $\text{LiPF}_6$ 等のリチウム塩を電解質塩として溶解させたものが使用されている。

## 【0008】

【発明が解決しようとする課題】 ところで、一般に、電池では、その内部抵抗によって内在するエネルギーの一部が消費される。したがって、充電したエネルギーを効率よく使用するためには、内部抵抗は低ければ低いほど望ましいと言える。

【0009】 電池の内部抵抗は、主に活物質内の抵抗と、活物質粒子と電解液との界面に発生する抵抗(以下、界面分極抵抗と称する)とに由来し、これらの抵抗を合わせたものが電池全体の内部抵抗に相当する。

【0010】 ここで、先に正極活物質として例示したリチウム含有複合酸化物では、この界面分極抵抗が経時的に増加するといった現象が見られる。なかでもNiを含有するリチウム含有複合酸化物は、容量が大きく比較的安価であるといった長所を有するものの、 $\text{LiCoO}_2$ 等に比べてこの界面抵抗の経時的増加が比較的大きい傾向が短所の一つになっている。

【0011】 そこで、本発明はこのような従来の実情に鑑みて提案されたものであり、界面分極抵抗の経時的な増加が少ない正極活物質を提供することを目的とする。また、そのような正極活物質を用いることで、内部抵抗が小さく充電エネルギーが効率良く使用される非水電解質二次電池を提供することを目的とする。

## 【0012】

【課題を解決するための手段】 上述の目的を達成するために、本発明者等が鋭意検討を重ねた結果、Niを含有するリチウム含有複合酸化物の表面近傍で、固体状態としてCo, AlまたはMnのいずれかをNiに対して高濃度に存在せしめるようにすると、この複合酸化物における経時的な界面分極抵抗の増加が抑えられるとの知見

を得るに至った。

【0013】本発明の正極活物質は、このような知見に基づいて完成されたものであって、 $LiNi_xM_yO_z$ （但し、 $M$ は $Al$ 、 $Mn$ 、 $Fe$ 、 $Ni$ 、 $Co$ 、 $Cr$ 、 $Ti$ 、 $Zn$ 、 $P$ 、 $B$ から選ばれる少なくとも一種の元素を表し、 $x$ は $0 < x \leq 1$ 、 $y$ は $0 \leq y < 1$ である）で表される複合酸化物粒子の表面を、 $Co$ 、 $Al$ 、 $Mn$ の少なくともいずれかを含有する化合物によって被覆処理してなっている。

【0014】この複合酸化物粒子表面を被覆するために使用する化合物としては、具体的には $Co$ 、 $Al$ 、 $Mn$ のいずれかを含有する金属アルコキシド等が挙げられる。なお、被覆処理に用いる化合物としては $Co$ を含有する化合物が好適である。

【0015】複合酸化物粒子表面を、これら化合物によって被覆処理すると、粒子表面に $Co$ 、 $Al$ 、 $Mn$ を含有する化合物が付着したかたちになり、複合酸化物粒子の表面における $z/(x+z)$ （但し、 $x$ は $Ni$ の原子組成比であり、 $z$ は $Co$ 、 $Al$ 、 $Mn$ の原子組成比の合計である。ここではこの値を $D(s)$ とする）が、複合酸化物粒子全体における $z/(x+z)$ （ここではこの値を $D(b)$ とする）よりも大なる値となる。なお、特に、処理用の化合物として $Co$ を含有するものを用いる場合には、 $D(s)$ は $1 \geq D(s) > 0.3$ であるのが望ましい。

【0016】

【発明の実施の形態】以下、本発明の具体的な実施の形態について説明する。

【0017】本発明の正極活物質は、 $LiNi_xM_yO_z$ （但し、 $M$ は $Al$ 、 $Mn$ 、 $Fe$ 、 $Ni$ 、 $Co$ 、 $Cr$ 、 $Ti$ 、 $Zn$ 、 $P$ 、 $B$ から選ばれる少なくとも一種の元素を表し、 $x$ は $0 < x \leq 1$ 、 $y$ は $0 \leq y < 1$ である）で表される複合酸化物粒子の表面が、 $Co$ 、 $Al$ 、 $Mn$ の少なくともいずれかを含有する化合物によって被覆処理されてなっている。すなわち、上記正極活物質は、 $Ni$ を含有するリチウム複合酸化物粒子表面に、 $Co$ 、 $Al$ または $Mn$ を含有する化合物が付着し、これによって粒子が表面改質されたかたちになっている。

【0018】このような表面改質が施された複合酸化物粒子では、表面に $Co$ 、 $Al$ または $Mn$ を含有する化合物が付着した分、表面において $Ni$ の占める割合が減少している。この $Ni$ の占める割合が減少したことで、界面分極抵抗の経時的増加が抑えられる。したがって、高容量、安価であるといった $Ni$ を含有する複合酸化物粒子の長所を備えながら、しかも電池の内部抵抗を増大させず、正極活物質として優れた特性が得られる。

【0019】処理用の化合物としては、例えば $Co$ 、 $Al$ または $Mn$ の金属アルコキシド等が挙げられる。このうち、例えば $Co$ アルコキシドによって複合酸化物粒子の表面改質を行うには、 $Co$ アルコキシドを溶解した表

面処理液に、被処理体となる複合酸化物粒子を投入、攪はん後、1日程度保存する。保存中に、複合酸化物粒子表面には $-O-Co-O$ の結合が生成し、 $Co$ 濃度の高い層が形成される。保存後、上澄液を捨て、残存粒子を溶媒で数回洗浄する。そして、この粒子を、乾燥することによって表面改質された複合酸化物粒子が得られる。 $Al$ アルコキシド、 $Mn$ アルコキシドによる表面改質もこれに準じて行われる。

【0020】また、処理用の化合物としては、 $Li$ を含んだもの、すなわち $Li$ と $Mn$ 、 $Al$ あるいは $Co$ の複合化合物であっても良い。

【0021】なお、処理用の化合物としては $Co$ を含有するものを用いるのが望ましい。 $Al$ あるいは $Mn$ では、複合酸化物粒子に固溶した場合に電池の容量を若干減少させる方向に働くが、 $Co$ の場合には電池の容量をほとんど減少させないからである。

【0022】このようにして表面改質が行われた複合酸化物粒子では、 $Co$ 、 $Al$ あるいは $Mn$ の濃度が、粒子全体よりも粒子表面において大きくなる。すなわち、表面における $z/(x+z)$ （但し、 $x$ は $Ni$ の原子組成比であり、 $z$ は $Co$ 、 $Al$ 、 $Mn$ の原子組成比の合計である）を $D(s)$ 、粒子全体における $z/(x+z)$ を $D(b)$ としたときに、 $D(s)$ の値が $D(b)$ の値よりも大なる値になる。なお、特に、処理用の化合物として $Co$ を含有するものを用いる場合には、 $D(s)$ の値は $1 \geq D(s) > 0.3$ であるのが望ましい。 $D(s)$ が $0.3$ 以下である場合には、複合酸化物粒子の界面抵抗の経時的増加を十分に低めることができない。

【0023】なお、この $D(s)$ 、 $D(b)$ はそれぞれ以下のようにして求められる値である。

【0024】 $D(s)$ の測定：0.1M HCl水溶液を50cc秤量し、常温下でこのHCl水溶液に粉体500mgを投入し、室温23℃下、5分間浸漬する。これにより、粉体の表面が酸によって溶解される。次に、HCl水溶液から溶解せずに残存した残渣粉末を除去する。そして、上澄液として残ったHCl水溶液のみをICP-AES (inductively coupled plasma-atomic emission spectroscopy) で分析し、溶液中に存在する $Ni$ と、 $Co$ 、 $Al$ または $Mn$ の量比を測定し、その測定量に基づいて $z/(x+z)$ を算出する。

【0025】 $D(b)$ の測定：1M HCl水溶液に、粉体500mgを投入し、粉体全体を溶解させる。そして、粉体を溶解させたHCl水溶液をICP-AESで分析し、溶液中に存在する $Ni$ と、 $Co$ 、 $Al$ または $Mn$ の量比を測定し、その測定量に基づいて $z/(x+z)$ を算出する。

【0026】以上のような表面改質が施された複合酸化物粒子は、非水電解質二次電池の正極に用いられる。

【0027】上記複合酸化物粒子で正極を形成するに

は、この複合酸化物粒子と導電剤及結着剤を混合して正極合剤を調製し、この正極合剤を所望の電極形状に圧縮成型する。ここで、導電剤や結着剤は、この種の電池で通常用いられているものがいずれも使用可能である。

【0028】また、上記正極と組み合わせて用いられる負極及び非水電解液も、やはりこの種の電池で用いられているものであって良い。

【0029】例えば負極の活物質としては、金属リチウムまたはリチウム-アルミニウム合金等のリチウム合金の他、リチウムをドーブ・脱ドーブすることが可能な材料が使用される。リチウムをドーブ・脱ドーブすることが可能な材料としては、例えば、熱分解炭素類、コークス類（ピッチコークス、ニードルコークス、石油コークス等）、グラファイト類、ガラス状炭素類、有機高分子化合物焼成体（フェノール樹脂、フラン樹脂等を適当な温度で焼成し炭素化したもの）、炭素繊維、活性炭等の炭素質材料、あるいはポリアセチレン、ポリピロール等のポリマー等を使用することができる。

【0030】このような炭素質材料やポリマーで負極を形成するには、これら材料と結着剤を混合して負極合剤を調製し、この負極合剤を所望の電極形状に圧縮成型する。

【0031】一方、非水電解液の非水溶媒としては、例えばプロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ビニレンカーボネート、γ-ブチロラクトン、スルホラン、1, 2-ジメトキシエタン、1, 2-ジエトキシエタン、2-メチルテトラヒドロフラン、3-メチル-1, 3-ジオキソラン、プロピオン酸メチル、酪酸メチル、ジメチルカーボネート、ジエチルカーボネート、ジプロピルカーボネート等を使用することができる。特に、電圧に安定な点から、プロピレンカーボネート、ビニレンカーボネート等の環状カーボネート類、ジメチルカーボネート、ジエチルカーボネート、ジプロピルカーボネート等の鎖状カーボネート類を使用することが好ましい。なお、これら非水溶媒はそれぞれ単独で使用しても2種類以上を組み合わせ使用しても構わない。

【0032】非水溶媒に溶解させる電解質塩としては、\*

\*  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  等を使用でき、このうち特に  $\text{LiPF}_6$  や  $\text{LiBF}_4$  を使用することが好ましい。

【0033】なお、この電池では、非水電解液の代わりに固体電解質を用いるようにしても良い。

【0034】また、電池の形状は特に限定されず、円筒型、角型、コイン型、ボタン型等の種々に形状にすることができる。

【0035】

【実施例】以下、本発明の実施例を実験結果に基づいて説明する。

【0036】実施例1

次のようにして正極活物質を生成した。

【0037】まず、以下に示す複合酸化物粒子及び表面処理液を用意した。

【0038】複合酸化物粒子（被処理体）： $\text{CoO}$ ,  $\text{NiO}$  及び  $\text{LiOH} \cdot \text{H}_2\text{O}$  を、 $\text{Li}:\text{Ni}:\text{Co}=1:0.8:0.2$  (mol比) となるように混合し、大気中、温度  $700 \sim 800^\circ\text{C}$  で10時間加熱処理することで得られた  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  粉末  
表面処理液： $\text{Co}$  イソプロポキシド [ $\text{Co}(\text{O}-i-\text{C}_3\text{H}_7)_2$ ] を、 $1\text{g}$  ( $5.6 \times 10^{-3}\text{mol}$  相当量) 秤取り、2-エトキシエタノール ( $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$ )  $100\text{cc}$  に溶解した  $\text{Co}$  アルコキシド溶液  
窒素雰囲気下、上記表面処理液に複合酸化物粒子  $2\text{g}$  を投入し、混合攪はんした後、24時間常温で保存した。保存後、上澄液を捨て、残存粒子を2-エトキシエタノールで数回洗浄した。そして、この粒子を、乾燥後、大気中で  $300 \sim 800^\circ\text{C}$  の温度にて加熱することによって表面改質された複合酸化物粒子（正極活物質）を得た。

【0039】なお、未処理の複合酸化物粒子と表面処理が施された複合酸化物粒子について、 $0.1\text{MHC1}$  あるいは  $1\text{MHC1}$  の溶解試験によって  $D(s)$ ,  $D(b)$  を測定した。その結果を表1に示す。

【0040】

【表1】

	$D(s)$	$D(b)$
処理済複合酸化物粒子	0.34	0.25
未処理複合酸化物粒子	0.26	0.25

【0041】表1に示すように、表面処理が施された複合酸化物粒子は、未処理の複合酸化物粒子よりも  $D(s)$  の値が増加している。このことから、この表面処理によって複合酸化物粒子表面の  $\text{Co}$  濃度が増加したことが確認された。

【0042】次に、以上のようにして表面改質がなされた複合酸化物粒子を正極活物質としてコイン型電池を作製した。

【0043】上記複合酸化物粒子90重量部にグラファイト7重量部及びフッ素系高分子バインダー3重量部を

加え、ジメチルホルムアミド (DMF) とともに混合することで正極合剤を調製した。この正極合剤を十分乾燥することで溶媒であるDMFを完全に揮発させた後、その約60mgを秤取り、加圧成型することで、表面積約2cm<sup>2</sup>の円盤状の正極電極を作製した。

【0044】一方、負極は、Li圧延金属を円盤状に打ち抜くことで作製した。

【0045】なお、この負極のLi量は正極の最大充電能力の数100倍であり、正極の電気化学的性能を制限するものではない。

【0046】以上のようにして作製された正極、負極をそれぞれ正極缶、負極缶に収納し、セパレータを間に挟んで積層した。そして、缶内にLiPF<sub>6</sub>をプロピレンカーボネート (PC) に溶解させた電解液を注入し、正極缶及び負極缶をガスケットを介してかしめ密閉することでコイン型電池を作製した。そして、この電池について、充放電電流密度0.5mA/cm<sup>2</sup>なる条件でOCV (開回路電圧) が4.2Vになるまで充電した。

#### 【0047】実施例2

複合酸化物粒子の表面処理液に溶解する金属アルコキシドとしてAl (OCH<sub>3</sub>)<sub>3</sub>を使用したこと以外は実施例1と同様にして正極活物質を生成し、コイン型電池を作製した。そして、この電池について、充放電電流密度0.5mA/cm<sup>2</sup>なる条件でOCV (開回路電圧) が4.2Vになるまで充電した。

#### 【0048】実施例3

複合酸化物粒子の表面処理液に溶解する金属アルコキシドとしてMn (O-i-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>を使用したこと以外は実施例1と同様にして正極活物質を生成し、コイン型電池を作製した。そして、この電池について、充放電電流密度0.5mA/cm<sup>2</sup>なる条件でOCV (開回路電圧) が4.2Vになるまで充電した。

#### 【0049】比較例1

表面処理を施していない複合酸化物粒子をそのまま正極活物質として使用したこと以外は実施例1と同様にしてコイン型電池を作製した。そして、この電池について、充放電電流密度0.5mA/cm<sup>2</sup>なる条件でOCV (開回路電圧) が4.2Vになるまで充電した。

【0050】以上のようにして作製された電池について、複素インピーダンス測定を12時間毎に行い、求め

られるCole-Cole plotより正極表面における界面分極抵抗を見積もった。なお、複素インピーダンスの測定条件は以下の通りである。

【0051】測定使用機種: HP4192A Impedance Analyzer

温度: 常温 (23℃)

周波数範囲: 0.5Hz~1000Hz

印加バイアス電圧: 4.2V

最大電流: 10mA

10 測定間隔: 12時間毎

求められた界面分極抵抗の経時変化を図1に示す。なお、図1において、縦軸は、測定開始からt時間後の界面分極抵抗R<sub>t</sub>を、測定開始時の界面分極抵抗R<sub>∞</sub>で規格化した値である。

【0052】図1からわかるように、Co, AlまたはMnの金属アルコキシドによって表面処理が施された複合酸化物粒子を正極に用いた実施例1~実施例3の電池は、未処理の複合酸化物粒子を正極に用いた比較例1の電池に比べて、正極表面における界面分極抵抗の経時的な増加が抑制されている。

【0053】このことから、Niを含有する複合酸化物粒子をCo, Al, Mnを含む化合物で処理することは、非水電解質二次電池において、当該複合酸化物粒子と電解液との間の界面分極抵抗が増大し難いものとする上で有効であることがわかった。

#### 【0054】

【発明の効果】以上の説明からも明らかなように、本発明の正極活物質は、LiNi<sub>x</sub>M<sub>y</sub>O<sub>2</sub> (但し、MはAl, Mn, Fe, Ni, Co, Cr, Ti, Zn, P, Bから選ばれる少なくとも一種の元素を表し、xは0<x≤1、yは0≤y<1である) で表される複合酸化物粒子の表面を、Co, Al, Mnの少なくともいずれか一種を含有する化合物によって被覆処理してなっているため、高容量、安価であるとともに界面分極抵抗の経時的な増加が少ない。したがって、このような正極活物質を用いることで、内部抵抗が小さく、充電エネルギーが効率良く使用される非水電解質二次電池が実現できる。

#### 【図面の簡単な説明】

【図1】正極表面における界面分極抵抗の経時変化を示す特性図である。

### 正図における分極抵抗の時間依存性

